Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Tuning the reduction power of supported gold nanoparticle photocatalysts for selective reductions by manipulating wavelength of visible light irradiation

Xuebin Ke, Sarina Sarina, Jian Zhao, Xingguang Zhang, Jin Chang and Huaiyong Zhu*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Gold nanoparticles supported on CeO_2 were found to be efficient photocatalysts for three selective reductions of organic compounds at ambient temperatures, under irradiation of visible light; their reduction ability can be tuned by manipulating the irradiation wavelength.

The application of sunlight-driven photocatalytic process to synthesize fine organic chemicals achieved some promising progress. Titania (TiO_2) and silica-supported titania are active for photocatalytic oxidation of light alkanes and alkenes under ultraviolet (UV) irradiation at ambient temperature.[1] Furthermore, various methods have been developed to produce visible light photocatalysts.[2] Given that reduction is a major process for the synthesis of organic fine chemicals, it will be of great interest if photocatalytic reduction processes can be applied to synthesize fine chemicals under visible light. However, the synthesis of organic compounds via visible light photocatalytic reduction is even more challenging than that via visible-light photocatalytic oxidation. Currently there are a few sparse reports on this topic, which focus on the reduction of nitric-aromatic using cadmium sulphide or modified titania as photocatalysts.[3]

Recently, we found that the supported Au-NPs exhibit superior performance in the photocatalytic reduction of nitro-aromatic compounds to produce corresponding azo compounds under both visible and UV irradiation.[4] It highlights that such reduction process can be driven by sunlight. Au-NPs absorb visible light mainly due to the surface plasmon resonance (SPR) effect.[5] High product selectivity can be expected as the photocatalytic reductions are conducted at ambient temperature; the low reaction temperature reduces the formation of by-products. Besides, products that are unstable intermediates in the reaction under heating (e.g. thermal reaction), can be obtained in this way.

In the present study, we investigated three typical reduction processes on supported Au-NP photocatalysts, 3 wt% of Au-NPs on CeO_2 support (Au-NPs/CeO_2), under visible light: deoxygenation of epoxides to alkenes, reduction of ketones to alcohols, and hydrogenation of azobenzene to hydroazobenzene. These reduction reactions are important in organic synthesis and biological chemistry.[6]

Table 1. Performance of three photocatalytic reductions.

Substrate	Product	Photon efficiency	TON[b]	Conv.	Sel.
		0.4	41	19.7	87.5
		0.7	72	34.5	88.2
		1.4	140	67.4	85.5
	CO_2, H_2O		-	Dec.[c]	-
		0.3	27	13.1	90.9
		0.4	65	31	>99
		0.6	85.3	41	>99
		0.2	27	13	70
		1.5	54	40	78
		2.4	129	62	80
		0.2[a]	43.7	21	78

[a] Reaction conditions: 0.05 g catalysts, 0.4 mmol substrate in 24 ml of isopropanol. [b] It stands for turnover number and was calculated by the mole conversion of the reactant and mole gold content (2.84%, determined by Energy Disperse X-ray Spectrum). [c] the reactant decomposed to CO_2 and H_2O.

The Au-NP photocatalyst exhibited excellent activity for these syntheses under visible light irradiation as shown in Table 1. 19.7% of styrene oxide was converted to styrene in 16 h with a high selectivity above 87.5%. 31% of acetophenone transformed into benzyl ethanol with a selectivity of 99%. 40% of azobenzene was reduced to hydrazobenzene in 6 h with a selectivity of 78%. These reactions were also conducted in the dark with other experimental conditions unchanged – very low conversions of the reactants were observed. This indicates that the reduction reactions can be driven by visible light irradiation.

The reductions of the substrates with various substituted

functional groups were also investigated (see Table 1). The results indicate that the Au-NP photocatalyst can reduce a wide range of epoxides, azo compounds, and ketones in high photocatalytic efficiency, yielding the corresponding alkenes, hydrazo compounds and alcohols, respectively. Higher conversions were generally achieved for reactants with an aromatic ring than those without the ring, possibly due to the stronger affinity of aromatic reactants to the Au-NP surface. The photon efficiency of the reduction reactions is relative high. For example, the photonic efficiency was 1.5% of the Au-NPs/CeO_2 for azobenzene hydrogenation, exceeding that of the well-known TiO_2 photocatalyst under UV irradiation (efficiency <0.2%).[2,8] The high photon efficiency and product selectivity are important advantages for practical applications.

The size and dispersion of the Au-NPs should influence their catalytic performance, which can be readily tuned by adjusting the ratios of sodium borohydride to $HAuCl_4$ and $HAuCl_4$ to CeO_2 support. Fig. 1 shows the typical transmission electron microscopy (TEM) images of the catalysts, the mean sizes of the Au-NPs in the three samples were estimated to be 2 nm, 5 nm and 8 nm, respectively. The X-ray photoelectron spectroscopy (XPS) spectra of the photocatalysts (Fig. 1d) indicate that gold exists in the metallic state.

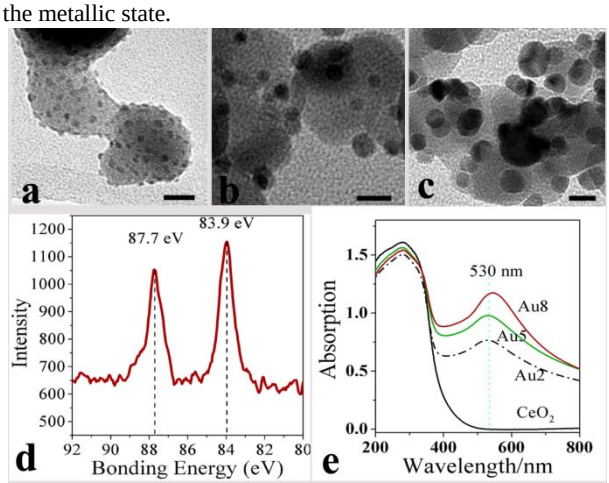

Fig. 1. TEM images of Au-NPs with different sizes and distributions on CeO_2 NPs. The length of the scale bars in the images is 10 nm. The mean size of Au-NPs in image (a) is 2 nm; in image (b) is 5 nm; and in image (c) is 8 nm. Panel (d) is the XPS spectra of 3% Au/CeO_2. Panel (e) is the UV-vis diffuse reflectance spectra of Au-NPs with different sizes on CeO_2.

An absorption band at about 530 nm is observed in the UV-vis spectra of the photocatalysts; this is the characteristic SPR absorption by Au-NPs as CeO_2 exhibits little absorption of light with wavelengths longer than 400 nm (Fig. 1e). Photocatalysts of different sizes of Au-NPs—and thus contents of gold—were also prepared. The light absorption by the sample with larger Au-NPs shifts to a longer wavelength and has higher intensity (Fig. 1e), indicating stronger SPR effect.[5] The strong light absorption is important to the photocatalytic performance, but the performance is also dependent on other factors, particularly the specific surface area of the Au-NPs. The larger the surface area is, the more active sites there are. The sample with smaller Au-NPs has a larger specific surface area but less intensive light absorption.[9] The sample with a mean gold particle size of 5 nm on CeO_2 exhibits the highest photocatalytic activity in reducing styrene oxide (Fig. S1).

A very interesting finding is the correlation between the irradiation wavelength and the reduction ability of the supported Au-NPs (Table S1). In experiments, glass filters were employed to block the irradiation below a certain wavelength (e.g. < 550 nm), this wavelength is called cut-off wavelength. When light with wavelength longer than 550 nm was used—by filtering out wavelength shorter than 550 nm—the reduction of azobenzene still proceeded even though the conversion (22%) decreased. This was similarly observed in the hydrogenation of acetophenone where the conversion decreased to 9%. However, the reduction of styrene oxide could not take place under such irradiation. Furthermore, when the cut-off wavelength was below 600 nm, the reduction of azobenzene still proceeded (20% of conversion), but acetophenone and styrene oxide could not be reduced.

A relationship between the cut-off wavelength of the irradiation and the reduction potentials of the reactants should exist. The reduction potentials of azobenzene, acetophenone and styrene oxide are –1.1 eV, –1.9 eV and –2.4 eV, respectively.[1,10] Correlating these reduction potentials with the reduction results acquired under irradiation of different cut-off wavelengths, it can be seen that a shorter cut-off wavelength is required to reduce a compound with a more negative reduction potential. Conduction electrons in the Au-NPs gain energy from the light absorption and the their distribution over the energy levels shifts to higher levels in the 6*sp* band.[4] The cut-off wavelength determines the energy of the excited electrons as well as their distribution over the high energy levels (Fig. 2). The shorter the wavelength is, the higher the energy of the excited electrons is (Table S1).

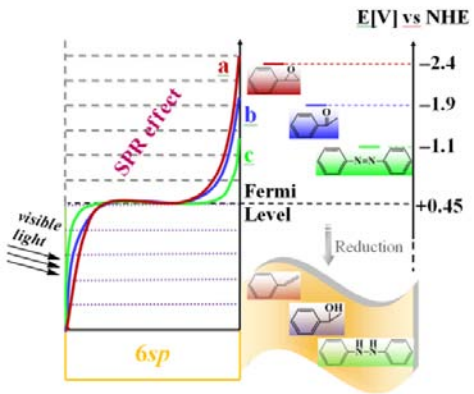

Fig. 2. Reduction potential of reduction reactions and schematic band structure of supported Au-NPs with glass filters of different cut-off wavelengths: (a) 420 nm; (b) 550 nm; (c) 600 nm.

The electrons excited by the light with wavelength longer than 600 nm are able to induce the reduction of azobenzene (reduction potential –1.1 eV), but cannot induce the reduction of more negative reduction potentials. Obviously the wavelength of the light determines the reduction power of the photocatalysts. This is rational from the view of thermodynamics that reductions with more negative reductive potential could not proceed because the reactant molecules could not gain the photo-excited electrons at lower energy levels. This may imply that the reactant molecules in the reduction with more negative reduction potentials can only gain the excited electrons of Au-NPs at the higher energy levels (Fig. 2), which are excited by light of shorter wavelength. As the SPR absorption of the Au-NPs is very weak in the range longer

than 650 nm (Fig. 1e), the conversion of all the three reactants is negligible (Table S1). This confirms again that the SPR absorption of Au-NPs is crucial for the catalytic activity.

In an attempt to clarify the influence of light irradiation intensity, the irradiation intensity was reduced from 0.4 to 0.3 and 0.15 W/cm^2, while other experiment conditions unchanged. We found that the conversion of styrene oxide decreased from 19.7% to 9.6% and 5.2%, respectively. Similar changes were observed for the reduction of the azoaromatics and the ketones (Table S2). These results further confirm that the reduction reactions were driven by visible light.

The Arrhenius equation was applied to derive the apparent activation energies of the reductions via photocatalytic and thermal catalytic processes. For one reduction reaction, the difference between the activation energies of the two processes indicates the contribution of light irradiation to reducing the apparent activation energy. The results of three reactions were showed in Fig. S2. Take acetophenone as an example, the activation energy is 43.7 kJ/mol for the photocatalytic reduction and 68 kJ/mol for thermal reduction. The difference between the two activation energies (24.3 kJ/mol) is the activation energy reduction by irradiation (Fig. S2). The relative reduction in the apparent activation energy due to the light irradiation, expressed in percentage of the apparent activation energy of the corresponding thermal process, $\Delta E_a/E_a$ (%), is also calculated for each reaction (Fig. S2). We found that the $\Delta E_a/E_a$ (%) is correlated with the values of the reduction potentials in the order of styrene oxide, acetophenone and azobenzene (Fig. 2). It means that only the energetic electrons beyond the reduction potential (excited by light with shorter wavelength) play a major role in activating reduction reaction. These observations reveal that the excited electrons at high energy levels in Au-NPs play a key role in the reactions.

Au-NPs were also loaded on TiO_2 and ZrO_2 and we found that for reduction of styrene oxide the selectivity to product styrene is moderately lower than that of the Au-NP on CeO_2 (Table S3). It appears that the support materials have limited impact on the conversion of photocatalytic reductions.

Given that the reductions were conducted in solvent of isopropanol that is a hydrogen-donor and the presence of KOH enhances the abstraction of hydrogen from isopropanol,[6c] it is possible that species of hydrogen atom bonded to Au-NP surface form and react with the reactant molecules on the Au-NPs,[4] meanwhile the reactant molecules may gain excited electrons from Au-NPs. The formation of Au-H species is confirmed (SI). The electrons remain in the excited state for up to 0.5-1 ps.[11] Hence, it is possible that a small number of excited electrons in Au-NPs gain sufficient energy to be captured by reactant molecules adsorbed on the Au-NPs under visible light irradiation, resulting in the photocatalysis. [12]

In summary, this study demonstrates that the Au-NP on CeO_2 is effective visible light photocatalyst for the reductions of organic compounds and its reduction power can be tuned by manipulating the irradiation wavelength. Such photocatalytic syntheses are sustainable and clean as production processes utilize sunlight for chemical synthesis.

Notes and references

School of Chemistry, Physics and Mechanic Engineering, Queensland University of Technology, Brisbane, Qld 4001, Australia. Fax: +61 7 3138 1804; Tel: +61 7 3138 1581; E-mail: hy.zhu@qut.edu.au

† Electronic Supplementary Information (ESI) available: Preparation of gold catalysts, influence of particle size, light intensity, and irradiation wavelength. See DOI: 10.1039/b000000x/

1 a) M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of Photochemistry*, 3rd ed., CRC Press, Boca Raton, 2006. b) X. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science* 2011, **331**, 746. c) J. Zhang, Q. Xu, Z. Feng, M. Li, C. Li, *Angew. Chem. Int. Ed.* 2008, **47**, 1766.

2 a) M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* 2007, **107**, 2725. b) R. Asahi, T. Morikawa, *Science* 2001, **293**, 269. c) M. Zhang, C. C. Chen, W. H. Ma, J. C. Zhao, *Angew. Chem. Int. Ed.* 2008, **47**, 9730.

3 a) B. Pal, T. Torimoto, K. Okazaki, B. Ohtani, *Chem Commun.* 2007, 483. b) A. Maldotti, L. Andreotti, A. Molinari, S. Tollari, A. Penoni, S. Cenini, *J. Photochem. Photobiol. A* 2000, **133**, 129.

4 a) H. Y. Zhu, X. B. Ke, X. Z. Yang, S. Sarina, H. W. Liu, *Angew. Chem. Int. Ed.* 2010, **49**, 9657. b) H. Y. Zhu, X. Chen, Z. F. Zheng, X. B. Ke, E. Jaatinen, J. C. Zhao, C. Guo, T. F. Xie, D. J. Wang, *Chem. Commun.* 2009, 7524.

5 a) S. Linic, P. Christopher, D. B. Ingram, *Nature Mater.* 2011, **10**, 911. b) P. Mulvaney, *Langmuir* 1996, **12**, 788. c) D. K. Roper, W. Ahn, M. Hoepfner, *J. Phys. Chem. C* 2007, **111**, 3636.

6 a) T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem. Int. Ed.* 2010, **49**, 5545. b) F. Zaccheria, F. Santoro, R. Psaro, N. Ravasio, *Green. Chem.* 2011, **13**, 545. c) F. Z. Su, L. He, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Chem. Commun.* 2008, 3531. d) A. Corma, H. Garcia, *Chem. Soc. Rev.* 2008, **37**, 2096. e) H. M. Nanjundaswamy, M. A. Pasha, *J. Chem. Res.* 2005, **12**, 772.

7 U. I. Gaya, A. H. Abdullah, *J. Photochem. Photobio. C* 2008, **9**, 1.

8 C. F. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, Weinheim, pp. 370-371, 1998.

9 a) S. Kohtani, E. Yoshioka, K. Saito, A. Kudo, H. Miyabe, *Catal. Commun.* 2010, **11**, 1049. b) K. Boujlel, P. Martigny, J. Simonet, *J. Electroanal. Chem.* 1983, **144**, 437.

10 S. Link and M. A. El-Sayed, *Int. Reviews in Physical Chemistry* 2000, **19**, 409.

11 a) H. Zhang, T. Watanabe, M. Okumura, M. Haruta, N. Toshima, *Nature Mater.* 2012, **11**, 49. b) H. Kominami, A. Tanaka, K. Hashimoto, *Chem. Commun.* 2010, **46**, 1287.